

Preparation and Polymerization of Cycloalkyl Acrylates^{1,2}

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In our earlier work³ it was found that all the alkyl polyacrylates studied had brittle points near room temperature, or lower. It was known that the presence of the cyclohexyl ring in the molecule caused a large rise in the softening point of polymethacrylates.⁴ Hence, it appeared of interest to prepare some cycloalkyl polyacrylates in the hope that they might be of use as rigid plastics.

The monomeric acrylates (Table I) were prepared by the alcoholysis of methyl or ethyl acrylate,⁴ and were polymerized in emulsion. Brittle

any sharp transition point. The small difference in the brittle points of the polymers is not considered significant.

The 4-cyclohexylcyclohexyl ester was a colorless solid, melting at 41°. Excepting monomeric hydroabietyl acrylate, which was slightly colored and exceedingly viscous, the esters were colorless, mobile, or slightly oily liquids having mild, pleasant, terpene-like odors.

The hydroabietyl and the 4-*t*-amyl- and 4-cyclohexylcyclohexyl polyacrylates appeared to be of low molecular weight. They were discolored and were extremely soft and tacky. Abnormally large amounts of catalyst were required to initiate their polymerization, indicating that some inhibitor re-

TABLE I
YIELDS, PHYSICAL CONSTANTS AND ANALYSES OF CYCLOALKYL ACRYLATES

Acrylate	Yield, %	Boiling pt. °C.	Mm.	n _D ²⁰	d ₄ ²⁰	Mol. refraction		Sapon. equiv.		Carbon, %		Hydrogen, %		Brittle pt. of polymer, °C.
						Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	
Cyclohexyl	77	75	11	1.4600	0.9796	42.75	43.12	154.2	155.0	70.1	70.2	16
Cyclohexyl ^a	..	182-184	Atm.	1.4673	1.0275	42.75	41.66
2-Methylcyclohexyl	70	69	5	1.4560	.9546	47.37	47.90	168.2	170.5	71.4	71.0	32
3-Methylcyclohexyl	78	74	6	1.4550	.9541	47.37	47.84	168.2	168.1	71.4	70.9	31
4-Methylcyclohexyl	85	55	2	1.4550	.9537	47.37	47.86	168.2	167.8	71.4	71.6	35
3,3,5-Trimethylcyclohexyl ^b	89	72	2	1.4542	.9292	56.60	57.31	196.3	204.1	73.4	73.6	10.3	10.4	48
3,3,5-Trimethylcyclohexyl ^c	50	40	0.2	1.4560	.9346	56.60	57.09	196.3	205.3	73.4	73.3	10.3	10.5	50
4- <i>t</i> -Amylcyclohexyl	85	95	1	1.4705	.9490	65.84	66.00	224.3	222.8	75.0	75.0	10.8	10.8	-8
4-Cyclohexylcyclohexyl ^d	86	115	1	1.4810 ^e	.9500 ^e	68.26	70.80 ^e	236.3	234.0	76.2	76.0	10.2	9.9	35
Hydroabietyl	25	177	0.3	1.5172	1.0181	102.53	102.42	344.5	349.2	28
3,3,5-Trimethylcyclohexyl ^f	88	79	1	1.4560	.9255	61.22	61.77	210.3	213.9	74.2	74.5	10.6	10.7	140

^a Reported by Ipatov, *J. Gen. Chem. (USSR)*, **15**, 639 (1945) [*C. A.*, **40**, 5697 (1946)]. ^b Made from alcohol of m. p. 35°. ^c Made from alcohol of m. p. 51°. ^d M. p., 41°. ^e At 50°. ^f Methacrylate made from alcohol of m. p. 35°.

points were determined as previously described.³ The one methacrylate was prepared (from methyl methacrylate) for comparison with the corresponding acrylate.

The two isomeric forms of 3,3,5-trimethylcyclohexanol (m. p. 35° and 51°) formed monomeric esters which showed small, but probably significant, differences in refractive index and density (Table I). Attempts to determine their melting points were indecisive; both samples became glass-like at about -50° without passing through

maintained in the monomer. All the other polymers were hard, white, granular solids, which were readily molded to form clear, colorless sheets.

3,3,5-Trimethylcyclohexyl polymethacrylate has been evaluated as a coating for optical lenses. It is reported to have outstanding resistance to water and to outdoor weathering.⁵

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(2) Presented before the Organic Chemistry Division of the American Chemical Society at the 117th National Meeting, Philadelphia, Pa., April, 1950.

(3) Rehberg and Fisher, *Ind. Eng. Chem.*, **40**, 1429 (1948).

(4) E. I. du Pont de Nemours and Co., *ibid.*, **28**, 1160 (1936).

(5) Cotes, Schulz, Levy and Wheatley, *Modern Plastics*, **25**, No. 11, 123 (1948).